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Industrial de Barcelona



Université Pierre  
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# MASTER THESIS

Discipline : Nuclear Engineering

presented by

**Guillem ANDREU PEDROSA**

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**Modelling and evaluating the consequences of the  
presence of  $O^{2-}$  in  $NaF-ZrF_4$  molten fluoride salt**

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supervised by Mathieu SALANNE

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Laboratoire PECSA  
(Physicochimie des Electrolytes, Colloïdes et Sciences Analytiques)  
Université Pierre et Marie Curie, Case Courrier 51  
Bâtiment F - 5<sup>e</sup> et 7<sup>e</sup> étage 4 place Jussieu  
75005 Paris

*Als meus pares,  
sense els quals mai hauria vist la llum.  
I a aquells que segueixent recordant-me cada dia que  
estar viu es ser afortunat, especialment a la Sílvia.*

*Sapere aude !*



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Therefore, I hope that the reader will very much enjoy this work as well as find it as immensely interesting as I think it is.



# Abstract

The framework of this study is the potential use of molten salts in the nuclear industry of the future. Those systems properties have been determined from finite temperature molecular dynamics simulations with a realistic representation of the interatomic interactions (the dipole-polarizable ion model, DIPPIM).

Among the quantities that can be obtained from molecular dynamics simulations, structural and dynamic properties hold particular interest for this work : those are mandatory to determine the various molten salts capabilities for being used as coolants in nuclear reactors, or the speciation of fission products in silicate glasses. This work has been particularly focused on the effect of adding small amounts of oxides in a fluorozirconate based molten salt. The formation of molecular ions based on strong Zr–O–Zr bonds results in an important medium-range ordering of the system and in a noticeable slowing of the dynamics of the ions, accompanied by an increase of the viscosity.

## Keywords

Fluoride ionic molten salts, fourth generation nuclear reactor, concentration of oxide, molecular dynamics, computer simulations, structural study, dynamical analysis, viscosity, diffusion, NaF–ZrF<sub>4</sub>.





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# Introduction

## 0.1 Generation IV Nuclear Reactors

The Generation IV Nuclear Reactors are a group of nuclear reactor designs still being investigated and not approved yet for commercial uses. Just some prototypes have been made and most of them are still in the theoretical phase of their conception. The research into this domain is based on seven technology goals [1] that should be reached by the time they start the commercial operating :

1. Improve nuclear safety by reducing the probability of a core damage accident by at least a factor of 10 compared to reactors presently in commercial operation.
2. Improve proliferation resistance through making the spread of nuclear weapons, fissile material, and weapons-applicable nuclear technology and information difficult.
3. Reduce as far as possible the waste production through the introduction of more efficient recycling schemes.
4. Minimize natural resource utilization.
5. Decrease the installation cost.
6. Diminish the cost to run such plants.
7. Provide electricity for lower cost than coal-burning plants.

The Molten Salt Fast Reactor (MSFR) [2] and the Advanced High-Temperature Reactor (AHTR) [3] are two concepts of Generation IV Nuclear Reactors.

## 0.2 Reactors involving molten salts

The MSFR is a type of nuclear fission reactor in which the primary coolant, which is also the fuel itself, is a molten fluoride salt. It differs from conventional water-cooled reactors in several aspects. One of the most important differences is the operation temperatures, that are much higher in MSFR while staying at low vapor pressure [4]. The system is pressure operating near atmospheric pressures, implying a reduction of the mechanical stress supported by the structure. That results in simplification of various aspects of the design, significant improvements of the safety [5] and the possibility to drastically reduce the amount of construction materials in the core.

The MSFR can be used efficiently for development of a Th – U breeder as well as for utilization of transuranium elements from the spent fuel of light water reactors and allows a continuous control of the fuel salt composition. If these facts are taken into account, it is seen that a highly efficient and technologically interesting balance of neutrons can be reached. [6]

Furthermore, it must be considered that a nuclear reactor core is a place where a large amount of heat is produced in a very limited volume. This must be absorbed and

transported quickly in an environment characterized by neutrons fluxes of high energy and high ionizing radiation levels. There are not much fluids able to effectively bear these constraints and allow rapid absorption and transfer of heat to the first heat exchanger. Molten salts exhibit the most appealing properties which explain why they have been taken in consideration very early in the nuclear energy production community. [6]

In the case of the AHTR, the molten salt is used as primary or secondary coolant only with no dissolved fissile materials or fission products, i.e. not as a fuel. [3]

The most relevant innovation in these nuclear reactors reside in the fuel fluid, but there are still several physical and technological aspects that must be studied to arrive to the working conditions. [7]

1. Elements constituting the fuel diluents should not absorb neutrons to anywhere near considerable extent.
2. The melting temperature of the salt composition should not be too high (less than 800 – 850 K) at sufficient concentrations of fissile and fertile materials.
3. A low vapor pressure at operating temperatures.
4. Chemical stability at working conditions and radiation resistance.
5. The absence of explosive exothermal reactions due to contact with water, air and other substances in the reactor.
6. Compatibility with construction materials and the moderator.
7. Transport properties of the fuel salt composition should ensure efficient removal of the heat generated at operating temperatures.
8. Possibility for the relatively simple extraction from the fuel salt composition of fission products absorbing neutrons in the core.

In view of the enumerated facts, a solvent whose components have a neutron little-absorber isotope species which concentration could be easily increased is needed. Lithium and sodium are capable to provide a fluid with such characteristics. As well, in the MSFR the system requires to reach the concentration level of fuel that guarantee the breeding of the fissile material in presence of fast or thermal neutrons. The molten fluoride mixture must have a satisfactory values of the heat capacity, the thermal conductivity and the viscosity at operating temperatures (800–1000 K). Finally, the solvent must not be physically affected by the presence of 1–2 mol% fission products and should avoid the formation of insoluble compounds under the operating conditions.

As will be seen in this work, the viscosity is an important parameter that will require an intense study.

The MSFR fuel should therefore be a mixture of the fissile and fertile material  $\text{UF}_4$  (or  $\text{PuF}_3$ ) and  $\text{ThF}_4$  respectively, dissolved over 20 mol% at the melting temperature and saturated vapor pressure (about 800 K and 10 Pa) in fluoride mixtures of Li, Be, Na and Th. [7] 20 mol%

For the AHTR, no fissile material is dissolved in the salt and the  $\text{LiF}-\text{BeF}_2$ ,  $\text{NaF}-\text{ZrF}_4$  or  $\text{LiF}-\text{NaF}-\text{KF}$  are the most promising candidates. [3]

### 0.3 The molten fluoride salt object of the work

It is important to consider that there is still several aspects on molten salt based reactors primary fluid that are not well established. This is the case for many basic physicochemical parameters, including the density, the viscosity, the heat capacity and the thermal conductivity of the salts under working conditions. In particular, the influence of oxide concentration has never been addressed. The prediction of such properties is therefore the object of several studies.

As shown, the interest in the development of the molten salt based reactors requires to perform theoretical and experimental studies of the molten salt mixtures containing alkali metals such as beryllium, zirconium, thorium, uranium, and plutonium fluorides. [8] Furthermore, in the AHTR there can be high amounts of zirconium. [9]

Between the large amount of compositions that could be used as described, a specific one with the Na as the alkaline element has been chosen. This study has been focused on a NaF–ZrF<sub>4</sub> molten fluoride salt with a composition of 66.7–33.3 mol% (that results in Na<sub>2</sub>ZrF<sub>6</sub>) with several concentrations in oxide.

#### 0.3.1 Pure NaF–ZrF<sub>4</sub>

It is well known [9] that experiments with molten fluoride salts have an added difficulty due to the high temperatures involved and their sensitivity to moisture and oxygen.

The specific structure of AF–ZrF<sub>4</sub> system, where A denotes the presence of an alkaline element such as Li, Na or K, compounds in the liquid state is nowadays being studied with several techniques such as the Extended X-Ray Absorption Fine Structure (EXAFS spectroscopy), molecular dynamics simulations, Raman spectroscopy. Recently a particular attention has been given to the systems with a 35 mol% of Zr. [10]

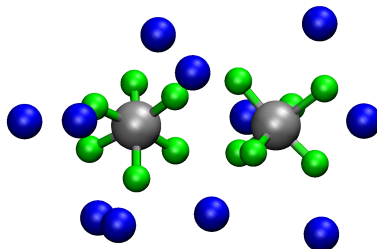


FIG. 1: Detail of the molten salt NaF–ZrF<sub>4</sub>.

The main results from these studies [11] concerns the speciation of zirconium with fluoride ions, for which evidences of five, six, seven and eight fold coordinated species at different percentages have been found. And the conclusion that the species tend to form no really large chains connected by their corners and/or their edges has also been reached.



# Notations

- DIPPIM : dipole-polarizable ion model.
- MSR : molten salt reactor.
- MSFR : Molten Salt Fast Reactor.
- AHTR : Advanced High-Temperature Reactor.
- XFTa : version a of the XFT definition of the potential.
- rdf : radial distribution function.
- K : kelvin.
- Pa : pascal.
- w.% : weight percentage.
- mol% : presence percentage.
- EXAFS : Extended X-Ray Absorption Fine Structure.
- NVT : constant number of atoms, volume (box lenght) and temperature.
- NPT : constant number of atoms, pressure and temperature.
- VMD : visual molecular dynamics.
- xmgrace : 2D graph plotting, advanced computation and exploration of data tool.
- msd : mean-squared displacements.
- $n_i$  : number of atoms of the species i.
- au : atomic units (bohr radius).





# Chapitre 1

## Methodology

### 1.1 Introduction

One of the most important goals to reach in the computer simulation experiences is to describe accurately the physical interactions which occur in condensed matter systems. So before starting any computer simulation it is important to bear in mind that a reliable interatomic force field for the substances that will be studied is needed. This potential has to be able to predict all the properties to a high degree of accuracy.

This work has been focused on purely ionic systems. Therefore, a dipole-polarisable ion model developed previously named DIPPIM has been used. Compared with other simpler models, this one gives accurate information to predict structural thermodynamic and dynamic properties. [12]

### 1.2 Molecular Dynamics

Molecular Dynamics simulation is a technique for computing the equilibrium and transport properties of a classical many-body system [13]. It has been used in this work because it offers the possibility of studying many properties of interest for the use of molten salts in the MSFR or AHTR. The term classical means that the nuclear motion of the constituent particles obeys the laws of classical mechanics; this methodology offers an excellent description for a large amount of materials without having to take into account any quantum effects explicitly. [14] [15]

In this technique the trajectories of the various atoms are determined numerically by solving the Newton's equations of motion for a system of interacting particles [16], where forces between the particles and potential energy are defined by molecular mechanics force fields as shown in the following equation,

$$F_i = m_i a_i \quad (1.1)$$

where  $m_i$  is the mass of the particle  $i$ ,  $a_i$  is the acceleration of the particle  $i$  and  $F_i$  is the total force on particle  $i$  as shown in the equation

$$F_i = -\frac{dV}{dr_i} \quad (1.2)$$

which derives from the potential energy  $V$ .

Molecular dynamics simulations are typically run for several nanosecond, and the thermodynamic averages are obtained as time averages using numerical integration of equation

$$\langle A \rangle = \frac{1}{M} \sum_{i=1}^M A(p^N, r^N) \quad (1.3)$$

where  $M$  is the number of time steps. A typical simulation cell is shown on Figure 1.1.

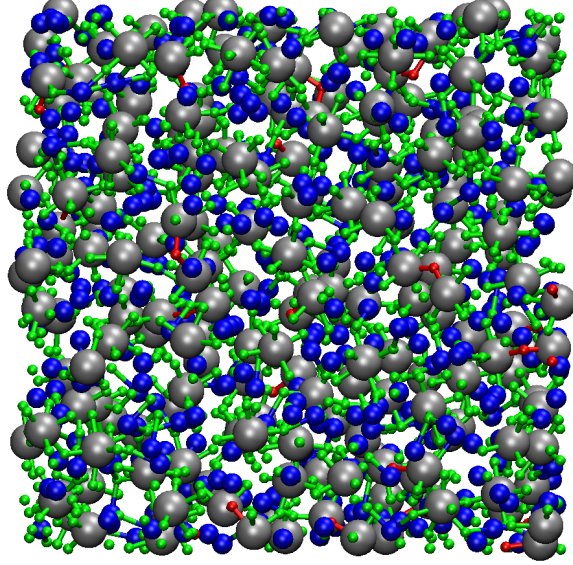


FIG. 1.1: NaF-ZrF<sub>4</sub> at 66.7–33.3 mol% and 30 oxygen ions simulation cell.

### 1.2.1 Periodic boundary conditions

The periodic boundary conditions (PBC) usually considered in Molecular Dynamics are based on the so-called minimum image convention. Its implementation leads to simulate a large system by modelling a small part that is far from its edge and to calculate which interaction should occur between pairs of particles separated by the minimum distance among the infinite number of images of the particles allowed by the PBC. [17]

The implementation used in the code to calculate the distance  $r$  between two particles (named 1 and 2) is shown in equation

$$\begin{cases} dx &= x1 - x2 \\ dy &= y1 - y2 \\ dz &= z1 - z2 \end{cases}$$

$$\begin{cases} dx &= dx - L \cdot \text{int} \left( dx \cdot \frac{1}{L/2} \right) \\ dy &= dy - L \cdot \text{int} \left( dy \cdot \frac{1}{L/2} \right) \\ dz &= dz - L \cdot \text{int} \left( dz \cdot \frac{1}{L/2} \right) \end{cases}$$

$$r = (dx^2 + dy^2 + dz^2) \quad (1.4)$$

where  $L$  is the length of the side of the simulation cell,  $x1, y1, z1$  are the positions of the particle 1,  $x2, y2, z2$  are the positions of the particle 2.

### 1.3 DIPPIM (DIPole-Polarizable Ion Model)

One of the most important ingredients in computer simulations is the construction of a reliable model for the system. Here we have chosen to use the DIPPIM, in which the interatomic interactions is the result of the superposition of four terms, which will now be described.

$$V = V^{qq} + V^{disp} + V^{rep} + V^{pol} \quad (1.5)$$

#### 1.3.1 Charge-charge interaction

First of all, there is the charge-charge interaction characterised by the formal charges of each ion.

$$V^{qq} = \sum_{i < j} \frac{q_i q_j}{r_{ij}} \quad (1.6)$$

Because the electrostatic potential describes long-ranged interactions, it is maximally efficient to decompose the interaction potential into a short-range component summed in real space and a long-range component summed in Fourier space as seen in equation

$$V^{qq}(r) = V_{sr}(r) + V_{lr}(r) \quad (1.7)$$

where  $V_{sr}(r)$  refers to the short-range and  $V_{lr}(r)$  to the long-range component.

In this way, the cutoff distance for the real space part of the Ewald sum and the short-range potential is calculated for ion pairs at distances lower than  $L/2$ . The value of the convergence parameter in the Ewald sum was set equal to  $5.6/L$  and  $8^3 k$  vectors were used for the reciprocal space part calculation of the force and potential energy. [10]

#### 1.3.2 Dispersion interaction

The dispersion interaction takes into account the dipole-dipole and dipole-quadrupole terms, which is always attractive.

$$V^{disp} = - \sum_{i < j} \left[ \frac{f_6^{ij}(r_{ij}) C_6^{ij}}{r_{ij}^6} + \frac{f_8^{ij}(r_{ij}) C_8^{ij}}{r_{ij}^8} \right] \quad (1.8)$$

In this equation it is important to stress the presence of the  $f_{ij}$  term that corresponds to the Tang-Toennies [18] dispersion damping function and it is used to describe the short-range corrections to the asymptotic dispersion term.

$$f_n^{ij}(r_{ij}) = 1 - e^{-d_{ij} r_{ij}} \sum_{k=0}^n \frac{(d_{ij} r_{ij})^k}{k!} \quad (1.9)$$

The parameter  $d_{ij}$  gives information about the range at which this correction occurs.

#### 1.3.3 Repulsion interaction

Following these terms, there is the short-range overlap repulsion term (which contains the Pauli principle of exclusion). These short-range repulsive interactions are approximated to an exponential-like term in the region of physical interatomic separations.

$$V^{rep} = \sum_{i < j} \frac{A^{ij} e^{-a^{ij} r_{ij}}}{r_{ij}^n} \quad (1.10)$$

$$V^{rep'} = \sum_{i < j} B^{ij} e^{-b^{ij} r_{ij}^2} \quad (1.11)$$

In some cases, an extra Gaussian term  $V^{rep'}$  has to be added to the overlap repulsion. Specially when the ions are highly polarized and in order to keep away from the polarization catastrophe that may occur for small anion-cation separations.

All the parameters were gathered from *Ab-Initio* calculations by a fitting procedure. Several validations that were made for NaF-ZrF<sub>4</sub> + O system are listed in the annexes. [12] [19]

### 1.3.4 Polarization

The last term is the polarization interaction effect, in this work only the dipolar polarization effect has been incorporated.

$$\begin{aligned} V^{pol} = & \sum_{i,j} \left[ q_i \mu_{j,\alpha} g_D^{ij}(r_{ij}) - q_j \mu_{i,\alpha} g_D^{ij}(r_{ij}) \right] T_\alpha^{(1)}(r_{ij}) \\ & - \sum_{i,j} \mu_{i,\alpha} \mu_{j,\beta} T_{\alpha\beta}^{(2)}(r_{ij}) \\ & + \sum_i \frac{1}{2\alpha_i} |\mu_i^2| \end{aligned} \quad (1.12)$$

$$g_D^{ij}(r_{ij}) = 1 - c^{ij} e^{-d^{ij} r_{ij}} \sum_{k=0}^4 \frac{(d^{ij} r_{ij})^k}{k!} \quad (1.13)$$

In this expression, for an ion  $i$  there is the  $\alpha_i$  that determines its polarizability,  $\mu_i$  is the induced dipole.  $T^{(1)}$  and  $T^{(2)}$  are the charge-dipole and dipole-dipole interaction tensors.

$$T_\alpha^{(1)}(r) = -r_\alpha / r^3 \quad (1.14)$$

$$T_{\alpha\beta}^{(2)}(r) = (3r_\alpha r_\beta - r^2 \delta_{\alpha\beta}) / r^5 \quad (1.15)$$

The potential used can be seen to contain several additional degrees of freedom, the induced dipoles, which describe the state of the electron charge density of the ions. They are calculated in a minimization procedure

$$\left( \frac{\partial V_{DIPPIM}^{pol}}{\partial \mu_\alpha} \right)_{(\mu_\alpha^N)} = 0 \quad (1.16)$$

which has to be performed at each time step.

## 1.4 Choosing the simulation cell composition

To determine which should be the amount of oxide dissolved in the molten salt, two comparisons have been made. The most relevant one was carried out with the PhD thesis of Olivier Pauvert [20] where the molten eutectic salt  $\text{ZrF}_4\text{-LiF}$  (21–79 mol%) was studied with addition of up to 20 mol% of  $\text{CaO}$ , which equals to a 15.34 % of oxygen over fluorine ratio ( $n\text{O}/n\text{F}$ ).

Another examination was performed to note the similarities between the molten salt of this work and the low-melting aluminium electrolytes  $\text{NaF-AlF}_3$  (55–45 mol%) where the effect of an addition of 2 wt.% of  $\text{Al}_2\text{O}_3$  was studied by Híves, J and Thonstad, J. [21]. That equals to a 1.92 % of oxygen over fluorine ratio.

This work has been started from pure  $\text{Na}_2\text{ZrF}_6$  and progressively replaced  $\text{F}^-$  ions by  $\text{O}^{2-}$  ones. The general formula of the system is  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$ .

The higher concentration of oxide has been reached with 200 atoms of oxygen in the simulation cell, that equals to  $n\text{O}/n\text{F}=12.50\%$  and 25.00 mol% of oxygen.

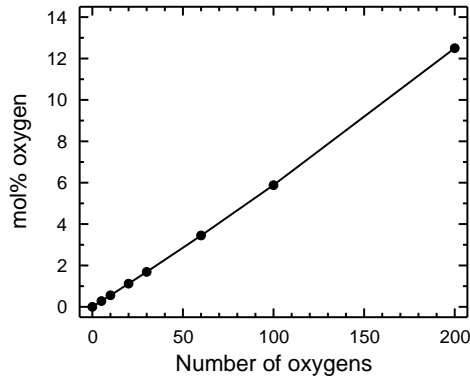


FIG. 1.2: Relation between the number of oxide ions and mol% of oxygen

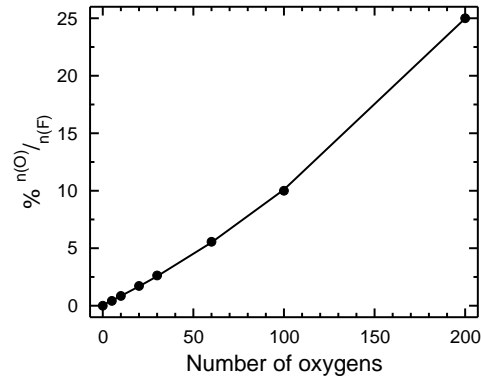


FIG. 1.3: Relation between the number of oxide ions and the ratio  $n\text{O}/n\text{F}$  (%)

Additional information about the number of atoms inside the simulation box is listed in the annexes.

## 1.5 General steps

To carry out the simulations, a strict procedure, determined thanks to previous works [9] and own experimentations, has been used :

1. The initial file with the positions and velocities of the ions must be adapted to simulate a sample with the number of oxygens aimed. In order to keep the system neutral, some fluorine ions have been removed from original lattice. It is important to emphasize that this exchange will be a potential source of instability for the initial simulations.
2. As far as an unstable structure is obtained, a stabilization simulation with a periodical rescaling of the velocities during 5 ps is required.
3. With the aim to achieve a volume equilibrated system, an NPT simulation (constant number of atoms, pressure and temperature) is realized during 100 ps.
4. Once fixed the length of the box, a short NVT (constant number of atoms, volume and temperature) simulation of 2 ps is executed to equilibrate further the sample.
5. Finally three successive production NVT simulations of 1 000 ps each are done, from which all the analysis have been performed.

It is important to stress that the values of density obtained in the third step agree well with experimental data for the oxygen-free sample [22]. When oxygen is present, no experimental data is available yet.

The input data of the simulations is provided in the annexes.

## 1.6 Analyzing the data

It must be taken into account that the huge quantity of data obtained must be analyzed. This data processing, despite being far from requiring the same computing resources than the production runs themselves, involve several processing methods. Those consist on inspecting, cleaning, transforming and modeling the information obtained, in order to draw conclusions of the work.

Here are listed some of the methodologies that have been used.

### 1.6.1 Radial distribution function

It is the ratio between the average number density calculated at a specific distance from any given atom and the density at the same distance that would be obtained in an ideal gas at the same overall density. It reflects correlations between the particles due to the intermolecular interactions.

It has a special interest because the results can be compared directly with neutron and X-ray scattering experiments and denote the similarities or differences between systems in theories of the liquid state.

### 1.6.2 Visualization

The molecular visualization computer program named Visual Molecular Dynamics (VMD) has been used for representing and analyzing the results of molecular dynamics simulations. It includes also tools for working with volumetric data, sequence data, and arbitrary graphical objects.

### 1.6.3 Analyzing the data numerically through *coord.x*

This program, improved from the previous version compiled by M. Salanne, deals with the numerical analysis of the information contained in the trajectory generated during the simulations. Its function is basically to read the positions in each step of the simulation, treat them numerically and display them in a statistically relevant format.

It allows to choose several kinds of analysis :

- Coordination analysis : shows in percentages how many ions of a specific species are coordinated to the other ones.
- Linkage state analysis : analyzes the bridges that three specific species create and present it in percentages.
- Linkage mechanism analysis : analyzes the bridges that a specific species has formed and display it in percentages.
- Angle analysis : analyzes and allows a representation discretized in steps of 1 degree of the angle formed by two species and a third one that will be the vertex.
- Sharing analysis : analyzes the corner, edge and face sharing of a specific species.
- Select coordination analysis : similar to the coordination analysis, but allows to restrict the statistical count to a group of atoms linked to a specific number of another concrete species.
- Select angle analysis : similar to the angle analysis, but allows to restrict the statistical count to the angle formed by a specific bridge formation. It has been shown to be extremely useful to characterize complexes.
- Select linkage state analysis : similar to the linkage state analysis, but allows to restrict the statistical count to a specific bridge formation. It has been shown to be extremely useful to characterize complexes.

An example of the input code of this program and the whole code of the program itself have been attached in the annexes.

### 1.6.4 Viscosity

Viscosity is the fundamental mechanism of momentum dissipation in a fluid. It is described at the macroscopic level by the general Navier-Stokes equation, shown in equation 1.17, which represent the balance of momentum in a fluid.

$$\rho \left( \frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \nabla \cdot \sigma + f \quad (1.17)$$

Where  $v$  is the flow velocity,  $\rho$  is the fluid density,  $p$  is the pressure,  $\sigma$  is the stress tensor, and  $f$  represents body forces per unit volume acting on the fluid and  $\nabla$  is the vector differential operator. [17]

At the microscopic level, viscosity arises because of a transfer of momentum between fluid layers moving at different velocities. The Green-Kubo expression for the shear viscosity  $\eta$  is shown in equation 1.18. [14]

$$\eta = \frac{1}{Vk_B T} \int_0^\infty dt \langle \sigma_{xy}(0) \sigma_{xy}(t) \rangle \quad (1.18)$$

### 1.6.5 Mean-squared displacements

The mean square displacement of atoms in a simulation can be easily computed by its definition as seen in equation 1.19.

$$MSD = \langle |r(t) - r(0)|^2 \rangle \quad (1.19)$$

Where  $\langle \dots \rangle$  denotes an averaging over all the atoms or, in the case that concerns this work, all the atoms in a given subclass.

The MSD provides information on the atomic diffusivity. In this work the system is a liquid, so MSD graphical representation grows with time and three different areas could be identified in its representation : the ballistic, the cage and the diffusion zone. It is important to stress that just the last one contains useful information to characterize the system behavior : the slope is used to calculate the diffusion coefficient  $D$ .

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle \quad (1.20)$$

The 6 in the above formula is the result of working in a three-dimensional system. [17]



# Chapitre 2

## Results

### 2.1 Structure analysis

The objective of this analysis is to determine quantitatively the structure of the molten fluoride salt and its alteration with the quantity of dissolved oxide ions. To achieve that, data from the positions, energies and velocities files must be analyzed and treated in order to obtain understandable information that could be interpreted.

#### 2.1.1 Definition of the first coordination shell

On a local scale, the molecular assemblage is divided in two zones that are characterized by the proximity to a central ion, the short-range structure, also known as the structure of the first coordination shell, and the medium-range structure.

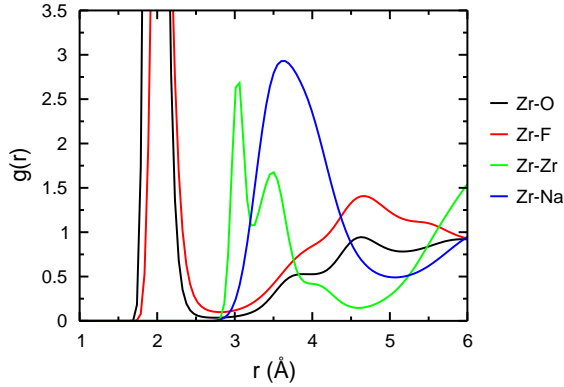


FIG. 2.1: Radial distribution functions  $g_{Zr-x}(r)$  for a concentration of 12.50 mol% of O. Note that the maxima  $g_{Zr-O}(r_{max})=21.1$  and  $g_{Zr-F}(r_{max})=8.7$  are not shown to make comparison clearer.

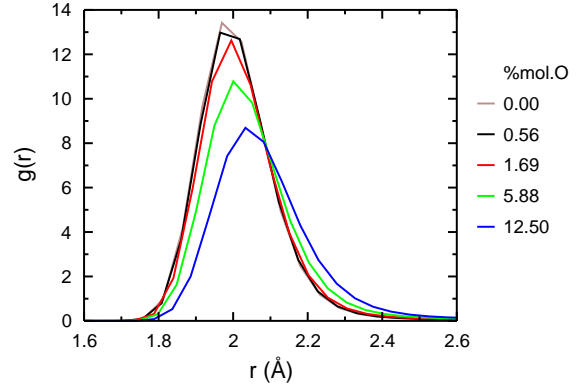


FIG. 2.2: Radial distribution function  $g_{Zr-F}(r)$  for the various compositions.

The information gathered for the radial distribution function provides an insight of what should be the studies to perform : which bridge formation examination should be analyzed in detail and which are the angles whose aperture will be modified by the oxygen presence between others.

Before considering the information of any analysis it could be established that the pure  $\text{Na}_2\text{ZrF}_6$  system will have a behaviour similar to what is observed in precedent studies [9] and [10].

A sample of the various radial distribution functions is represented in Figure 2.1 and Figure 2.2. A detailed observation of the first peak-zone provides the information needed to extract the first conclusions. In particular, we observe very strange Zr-F and Zr-O bonding.

In a molten salt, the radial distribution function generally takes shape of successive peaks separated by minima. Definitely, the evidence of which is the line that discriminates these anions that are coordinated with those that are not is found in the first off-peak zone and it is named the *cut-off* ( $R_{cut}$ ).

With the procedure detailed in the previous paragraph, the values of the  $R_{cut}$  have been read by direct inspection from the radial distribution functions. They are detailed in Table 2.1. The coordinated atoms are defined as those that are closer than the  $R_{cut}$ .

	O	F	Zr	Na
O	3.55	3.60	2.38	3.33
F	3.60	3.60	2.54	3.44
Zr	2.38	2.54	4.50	5.24
Na	3.33	3.44	5.24	5.40

TAB. 2.1: Values of  $R_{cut}$  (Å) that have been used to define the geometric criterion to calculate the coordination number of each ion.

### 2.1.2 Study of the first coordination shell

In previous studies based on pure  $\text{Na}_2\text{ZrF}_6$  the formation of several  $[\text{ZrF}_x]^{4-x}$  species has been demonstrated [9]. In this study, we observe that the evolution of these complexes is highly attached to the concentration of oxide solvated in the system.

From the Zr-O radial distribution function, a strong binding between zirconium and oxygen ions is also expected. The newly-formed complexes will therefore take the form  $[\text{ZrF}_x\text{O}_y]^{4-x-2y}$ . In a first step, the Zr-F and Zr-O coordination numbers (CN) have been calculated independently, these are shown on Figures 2.3 and 2.4.

In the case of a null concentration in oxide, the clear superiority of the complex  $[\text{ZrF}_6]^{2-}$  at about 88.2 % is observed (see left zone of Figure 2.3). The second most likely complex is  $[\text{ZrF}_7]^{3-}$  at about 11.1 % (not shown in the Figure). Such fluorozirconate anions can eventually, as seen in previous studies [10] in mixtures that are composed of similar species, be linked together through a bridging fluoride. The presence and evolution of these bridges has been studied in the medium-range structure study of this report.

If the situation at the highest presence of oxide is considered, an interesting distribution in the zirconium – fluorine coordination number is observed. The most likely CN is of 4 (48.0 %) and an approximate coexistence of the CN 3 at 19.5 % and CN 5 at 23.0 % is observed.

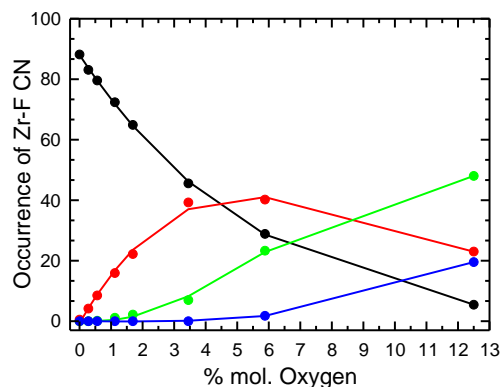


FIG. 2.3: Average formation of ZrF complexes with varying oxide concentration.

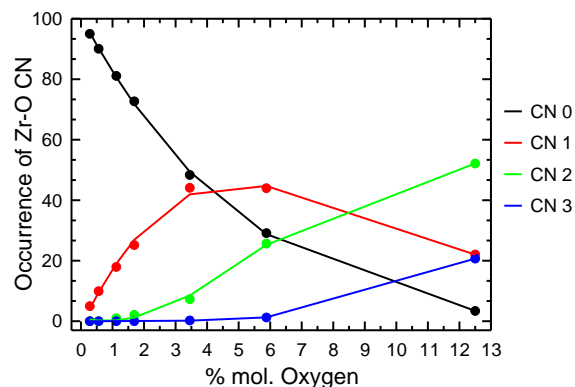


FIG. 2.4: Average formation of ZrO complexes with varying oxide concentration.

It is equally important to pay special attention when observing the evolution of the zirconium – oxygen coordination number with varying the oxide concentration, which is shown on Figure 2.4, and notice how a symmetric variation is observed. In particular, it must be stressed the major presence of the CN 2 at 52.1 % followed by the CN 1 and CN 3 at 22.1 % and 20.7 % respectively.

In order to clearly understand the relation between the presence of an oxide in the first coordination shell of each zirconium and the fluoride coordination of this species, a select coordination analysis restricted to one, two, three or four-oxygen zirconium-based complexes study has been made. This result is shown in Figures 2.5. It could therefore be concluded that, as in pure  $\text{Na}_2\text{ZrF}_6$ , the majority of the Zirconium ions have a total CN of 6.

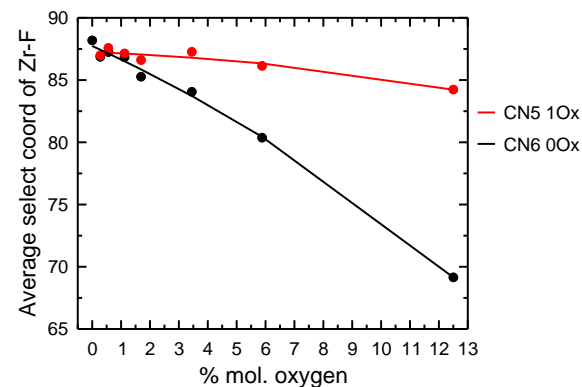
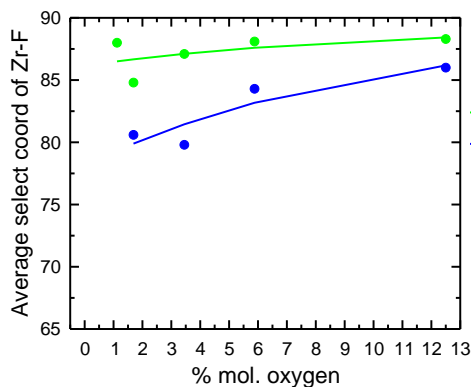


FIG. 2.5: Average formation of ZrF complexes restricted to those Zr that are zero, one, two or three oxygen coordinated with varying oxide concentration. Only the major concentration species is shown in each case.

### 2.1.3 Presence of bridging F and O ion

Once having seen that the number of fluoride and oxygen anions to which each zirconium is bonded changes considerably with the modifications of oxide concentration, the influence on the medium-range structure has to be studied.

A visual inspection shows that there is a trend of the fluoride and oxygen anions towards forming bridges between two cations of zirconium, as shown in Figures 2.6 and 2.7. The characteristics of these bridges, as the formed angle and the number of anions that connect the same zirconium, are shown to be dependent on the charge and polarizability of each species and the concentration of oxide in the system.

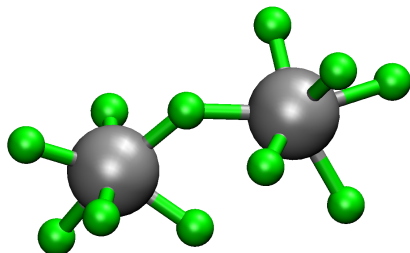


FIG. 2.6: Graphical representation of a fluoride bridge in molten  $\text{Na}_2\text{ZrF}_6$  represented in VMD.

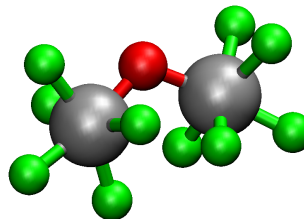


FIG. 2.7: Graphical representation of an oxygen bridge in molten  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  represented in VMD.

#### Fluoride bridges

Before anything else, it is important to note the vocabulary that has been utilized in this report and perceive the *one bridge* as a pair of zirconium ions connected together via one bridging anion, *two bridges* as a pair of zirconium ions linked together via two bridging anions and the same with the term *three bridges*. This terminology is used rather than the one based on corner, edge or face-sharing because it allows to distinguish  $\text{F}^-$  bridges and  $\text{O}^{2-}$  bridges.

In the pure system of  $\text{Na}_2\text{ZrF}_6$  at 1 200 K there is a high presence of the one fluoride bridge of about 63,9 %, followed by the zirconium ions that are linked with no fluoride bridges at about 26.1 % and those that are connected by two fluoride bridges at about 9.8 %, as seen in Figure 2.8<sup>1</sup>. It is interesting to give some attention to the way this bridge distribution changes with the increasing concentration of oxide.

Unequivocally, at the highest presence of oxygen the one fluoride bridge formation has been reduced to 37.2 %. Otherwise, the two fluoride bridges decreased to 4.1 % and the no fluoride bridge have been risen up to 58.6 %.

In order to understand further the geometry of fluoride bridges, an angle analysis has been done. The corresponding results are gathered on Figure 2.9.

A priori the differentiation of the influence of the number of bridges that results in the angle distribution seen in Figure 2.9 is not trivial. Everything would seem to indicate that there are more than one angle-type distribution, making the identification difficult.

1. The pairs of zirconium ions with no fluoride bridge fulfill the distance criterion  $r < 4.5 \text{ \AA}$ , but they do not share any common  $\text{F}^-$ .

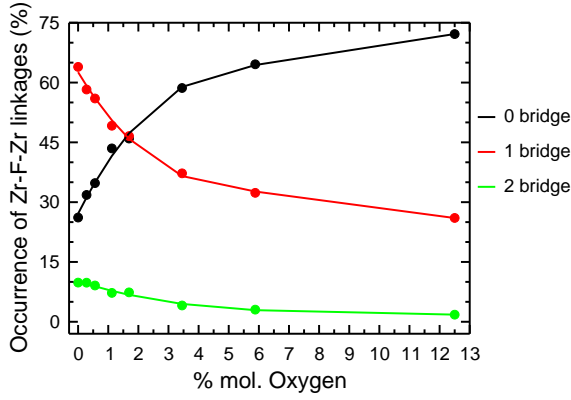


FIG. 2.8: Comparison of the average linkage state for the Zr-F-Zr bridges.

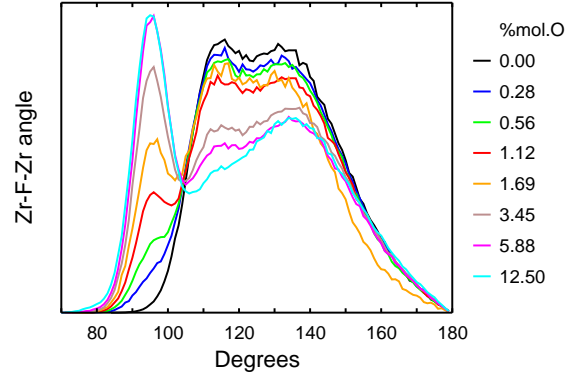


FIG. 2.9: Comparison of the average angle formation for the Zr-F-Zr bridges.

It has been supposed that the distributions shown in Figure 2.9 is the result of the addition of the angles formed by several complex as Zr-1F-Zr, Zr-2F-Zr and Zr-F/O-Zr between others. So a select angle analysis has been done and the corresponding results gathered on Figures 2.10 and 2.11.

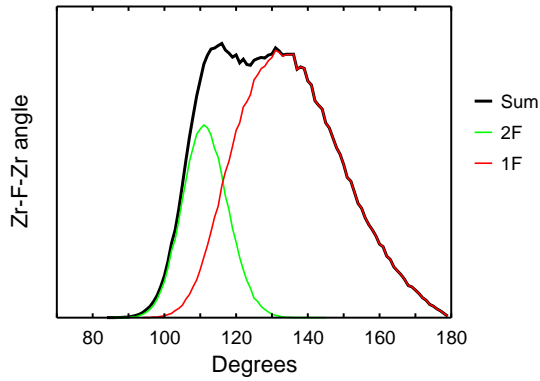


FIG. 2.10: Average select angle formation for the Zr-F-Zr bridges in pure molten  $\text{Na}_2\text{ZrF}_6$ .

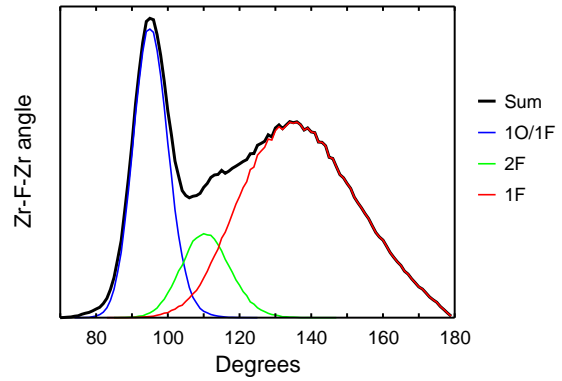


FIG. 2.11: Average select angle formation for the Zr-F-Zr bridges in molten  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  at the highest concentration of oxide.

Once differentiated the angle distributions and with the hypothesis in mind that the follow a Gaussian distribution, they have been fitted to the corresponding normal equation

$$f(x) = \frac{A}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}} \quad (2.1)$$

where  $\sigma$  controls the width of the Gaussian,  $\mu$  is the position of the center of the peak and  $A$  is the height of the curve's peak.

According to what has been seen, the angle distribution has been characterized, from left to right, at  $111.3^\circ$  and  $134.4^\circ$  in Figure 2.10. And  $95.5^\circ$ ,  $111.1^\circ$  and  $136.2^\circ$  in Figure 2.11. All of them with agreeable correlation coefficients above 0.95.

It is important to punctuate that this previous analysis has been done in order to differentiate the different angles formed by one specific species, in this case the fluoride, and two cations. In particular, the angle distribution from Figure 2.11 contains information about a particular contribution, which consists of a pair of zirconium ions being linked together by one fluoride and one oxygen.

### Oxygen bridges

Once seen the linkage formed by the fluoride anions, a similar study has been done with the oxide ions with the intention of characterize each complex that make up the system.

The first impression shows that, owing to the fact that the oxygen has both higher charge and polarizability, this species tends to form bridges that result in smaller Zr–O–Zr angles. It is worth noting that contrarily to  $F^-$  which can be either free, 1-fold or 2-fold coordinated to zirconium ions, the oxide anions are always linked to two zirconium ions (i.e. bridging).

If a linkage state and angle analysis is made to oxygen bridges, an interesting conclusion will be reached. See Figure 2.12. Contrary to what it is supposed to be logical after seen the fluoride linkage state analysis, not all the oxygen bridge formations obeys an exponential evolution and the one-bridge is shown to have a maximum at 4.18 mol% of oxide concentration, in which the presence of this kind of bridges is about 59.6 %.

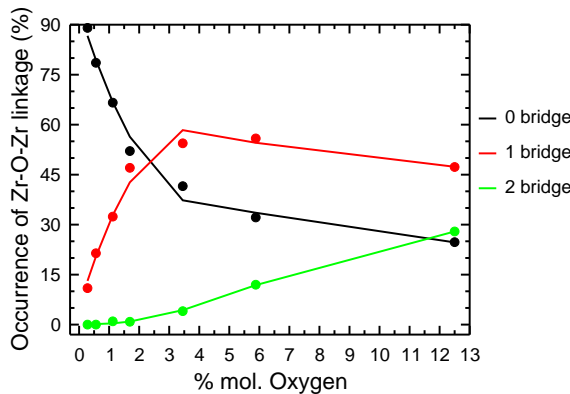


FIG. 2.12: Comparison of the average linkage state for the Zr–O–Zr bridges.

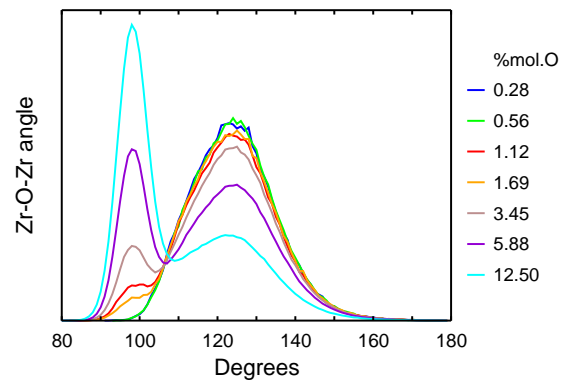


FIG. 2.13: Evolution of the average angle formation for the Zr–O–Zr bridges with oxide concentration.

From the linkage state analysis could be extracted that in the system with the smaller concentration of oxide, 10.9 % of the zirconium ions are linked by a one-oxygen bridge

are shown on Figure 2.12. Meanwhile at the highest concentration of oxide the major bridge formation is the one-oxygen bridge (47.3 %) followed by those that have no-oxygen bridges (24.7 %) and two-oxygen bridges (28.0 %). At higher concentrations of oxide, the two-oxygen bridge is the predominant.

As done in the case of the fluoride bridge formation, an angle analysis has been made in order to clearly understand the oxygen bridge formation. The corresponding results are gathered on Figure 2.13. And as has exactly seen in the previous analysis, we observe that there are more than just one angle distribution. Each of them can be fitted in a Gaussian as seen in the Equation 2.1 on page 29. With the objective of characterizing every distribution, a select angle analysis has been done. The results are shown in Figures 2.14 and 2.15 at 3.45 and 12.50 mol% of oxide concentration respectively.

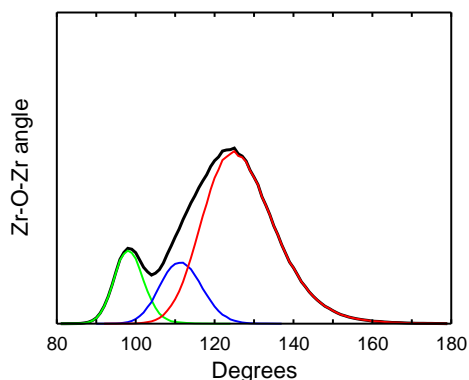


FIG. 2.14: Average select angle formation for the Zr-O-Zr complex of molten  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  at 3.45 mol% of oxide concentration.

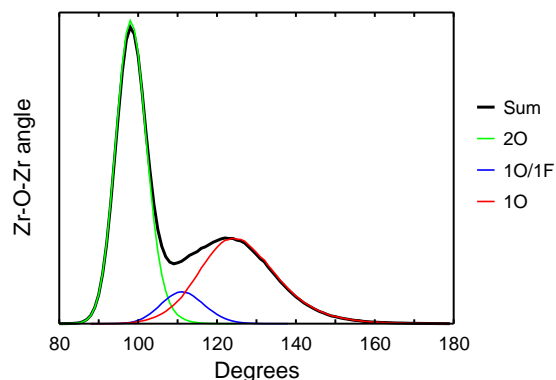


FIG. 2.15: Average select angle formation for the Zr-O-Zr complex of molten  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  at the highest concentration of oxide.

The oxygen angle distribution at an intermediate and at the highest concentration of oxygen has been characterized. From left to right in Figure 2.14 the average angles are of  $98.2^\circ$ ,  $111.4^\circ$  and  $126.0^\circ$  for 2O, 1O/1F and 1O respectively. In Figure 2.15 values of  $95.3^\circ$ ,  $111.3^\circ$  and  $125.2^\circ$  are obtained.

#### 2.1.4 Consequences on the medium range structure

The objective of this structure analysis chapter is to provide an idea of which is the structuring of the molten fluoride salt species and its alteration with the concentration of dissolved oxide ions. In this way, there is an output file that must be carefully studied to get an idea of which is the main change that the increasing concentration of oxide produces, namely the zirconium-zirconium radial distribution function.

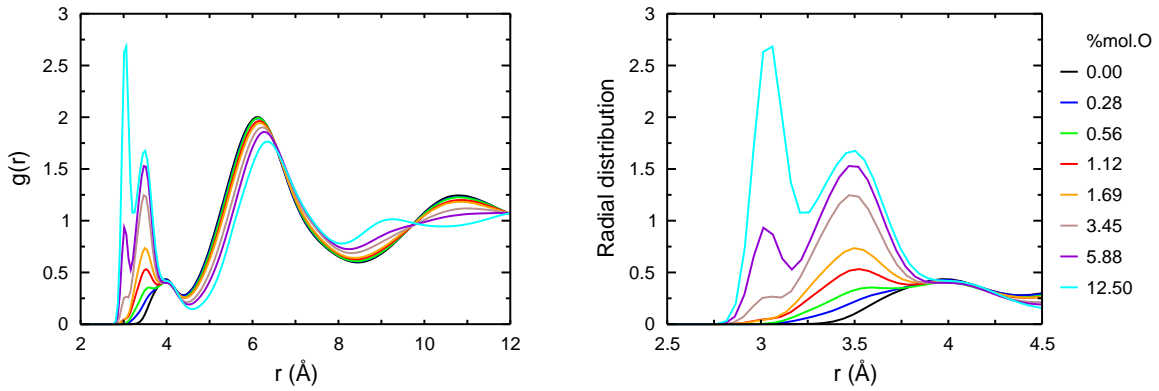


FIG. 2.16: Radial distribution function  $g_{Zr-Zr}(r)$  in molten  $Na_2ZrF_{6-2x}O_x$  mixtures of various concentrations (right : zoom on the first peak).

As seen in previous paragraphs, the increasing concentration of oxide in the system has a physical effect in the distance between the cations of zirconium. The result is clearly observable on the zirconium–zirconium radial function distribution as shown in Figure 2.16. A clusterization effect due to the formation of the first and the second bridges with oxygen ions is occurring.

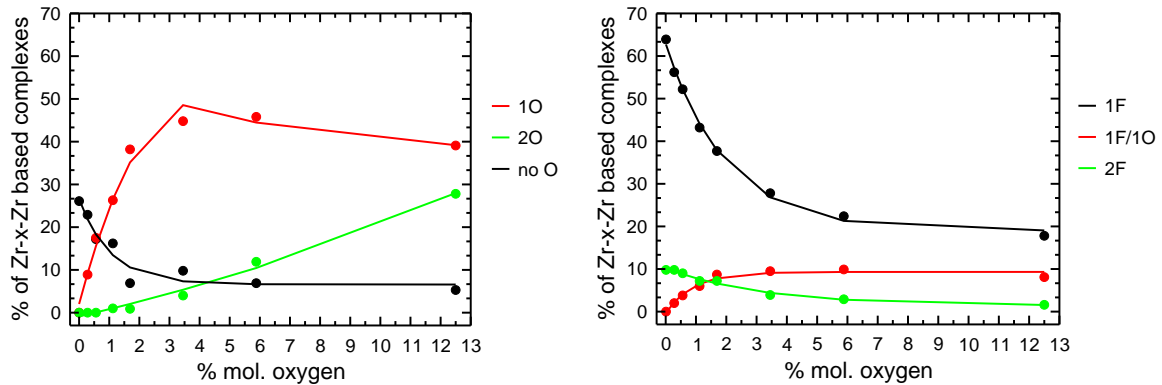


FIG. 2.17: Complexes evolution in the molten fluoride salt  $Na_2ZrF_{6-2x}O_x$  at 1200 K.

With the intention to describe the evolution of each complex that the sample contains, a particular analysis has been done combining the information of the select linkage state analysis and the select coordination analysis. The corresponding outcome is displayed on Figure 2.17.

And gathering the information named previously with the select angle distribution analysis, a characterization of each complex could be done. In this description of the compounds, see Table 2.2 at the highest concentration of oxide, the average predominance and the angle formed for each anion in the bridge could be extracted.



<b>Zr-x-Zr</b>	0 oxide	1 oxide	2 oxides
0 fluoride	5.3 % - -	39.1 % - 125.2°	27.8 % - 95,3°
1 fluoride	17.8 % 136.7° -	8.1 % 95.2° 111.3°	0.1 % 80,0° 80,1°
2 fluorides	1.6 % 110.5° -	0.1 % 87.8° 103.6°	0.0 % - -

TAB. 2.2: Summary table of the species that form each bridge at the highest concentration of oxide (12.50 mol%). Note that the upper angle in each cell refers to the one formed by the fluoride (Zr-F-Zr) and the lower one to the formed by the oxygen (Zr-O-Zr).

The characterization of the complexes at each concentration of oxide have been listed in the annexes.

Finally, in order to get an idea of which is the degree of polymerization, a generalized speciation analysis has been done. In this study, about 66 different compounds with a presence above 0.1 % have been found, and just a 15.8 % and 78.7 % of the one and two-oxygen bridges respectively are not part of a chain.

So there have been identified several complexes formed by a very wide range of combinations of zirconium and oxygen ions. But despite the existence of this large number of complexes, about 65 % are covered by just 9 complexes, which are detailed in the Table 2.3.

Occurrence (%)	Num of Zr	Num of Ox
22.0	2	2
8.9	3	3
7.5	2	1
4.6	3	2
4.5	4	4
4.3	3	4
3.6	4	5
3.4	5	6
2.7	10	12

TAB. 2.3: Summary of the number and composition of the most likely complexes in  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  molten fluoride salt at 1200 K and 12.50 mol% of oxide concentration. The sum of the occurrences equals 65 %.

## 2.2 Dynamic analysis

Once seen the most important structural alterations of the presence of oxide in the molten fluoride salt  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  at 1200 K, a study of the most relevant dynamical repercussions has been done.

It is interesting to observe how the diffusion of the zirconium and the oxygen tend to reach the same value above the concentration of 6 mol% of oxide concentration as seen in Figure 2.18. It could be easily understood if it is considered that these two species have the propensity for diffusing together once they are always linked by one or several oxide ions.

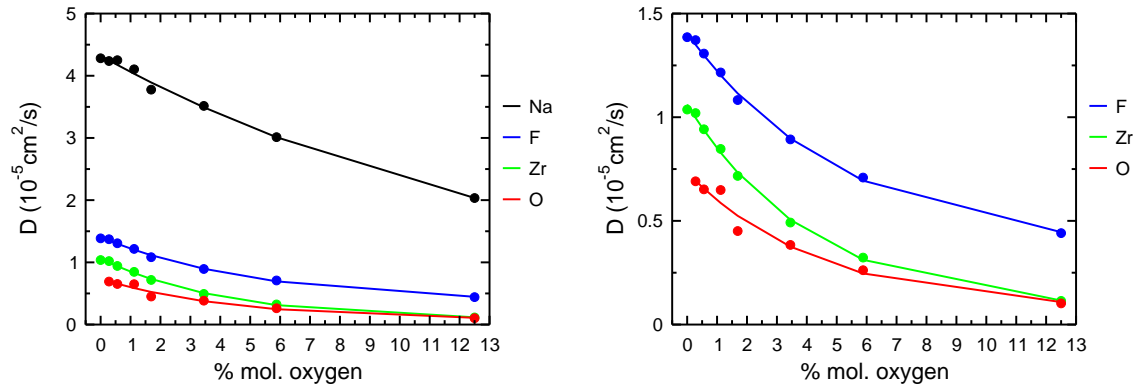


FIG. 2.18: Variation of the diffusion coefficient with the oxide concentration at 1200.

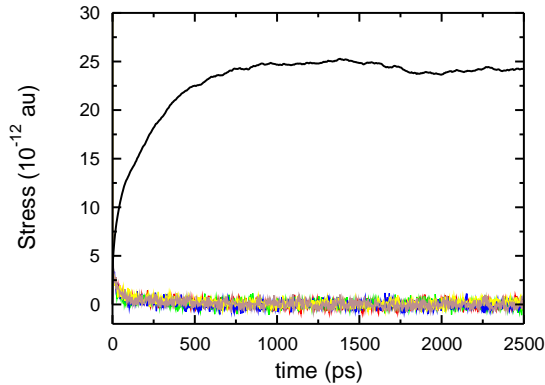


FIG. 2.19: Time evolution of the stress tensor correlation function at the highest concentration of oxide.

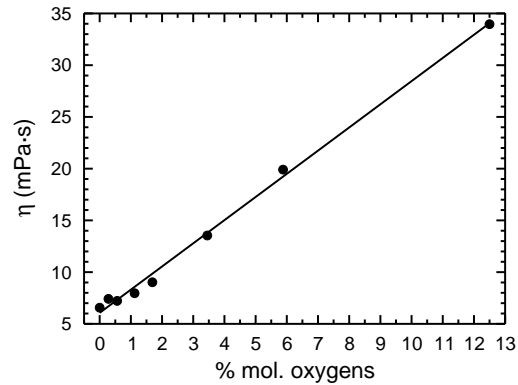


FIG. 2.20: Evolution of the viscosity of molten fluoride salt  $\text{Na}_2\text{ZrF}_{6-2x}\text{O}_x$  at 1200 K with the increasing concentration of solvated oxygen.

The integral of the stress tensor autocorrelation function, from which the viscosity is calculated in Figure 2.19 reaches a plateau value after about 1 000 ps, which represents the time scale for structural relaxation.

In order to obtain an approximate correlation of the viscosity of this molten fluoride salt depending on the temperature and the concentration of oxide in the interval from 0 to 12.50 mol% a regression to the obtained data has been fitted. The viscosity has a linear evolution with the increasing concentration of oxide as seen in the equation

$$\eta[mPa \cdot s] = A0 + A1 \cdot [Oxide] \quad (2.2)$$

where A0 is 6.069 mPa·s, A1 is 2.239 mPa·s/mol%O and  $[Oxyde]$  is the concentration of oxide in mol% of oxygen. This equation correlates with the data with a correlation coefficient of 0.998.



## Chapitre 3

# Conclusions

The local structure of zirconium, fluoride and oxide ions in a molten fluoride salt NaF–ZrF<sub>4</sub> (66.7–33.3 mol%) including different concentration of oxide at 1 200 K has been studied with molecular dynamics simulations. The different complexes have been characterized and their average presence compared for the various concentrations of oxide.

The zirconium–fluoride coordination number has been shown to be highly dependent of the concentration of oxide in the system. Furthermore, the presence of a polarizable ion as oxygen has shown to be a deciding factor in the "polymerization" of the system.

It has been shown that the physical properties of the fluoride molten salt Na<sub>2</sub>ZrF<sub>6–2x</sub>O<sub>x</sub> are strongly influenced by the quantity of solvated oxygen ions and their influence have been numerically determined in the viscosity and the diffusion.

Finally, the results obtained in this work show that if the application of this molten fluoride salt as primary coolant inside Nuclear Fission Reactors involving molten salts is considered, an additional pumping power will be needed in order to compensate the increasing viscosity of the fluid. Additional charge losses will have to be considered.

Furthermore, as far as natural circulation of the primary coolant it is supposed to be a passive security measure in this kind of Nuclear Power Plants, the influence that the viscosity could have in this phenomena should be studied.



# Annexe A

## Data and values

### A.1 Simulations characteristics.

Starting system : NaF–ZrF<sub>4</sub> (66.7 mol% – 33.3 mol%)

n O	n F	n Zr	n Na	% O/F	% mol.O	box.l[Å]	$\rho[g/cm^3]$
0	1200	200	400	0.00	0.00	31.52	2.665
5	1190	200	400	0.42	0.28	31.45	2.676
10	1180	200	400	0.85	0.56	31.44	2.672
20	1160	200	400	1.72	1.12	31.33	2.688
30	1140	200	400	2.63	1.69	31.09	2.740
60	1080	200	400	5.56	3.45	30.85	2.766
100	1080	200	400	5.56	3.45	30.38	2.844
200	1080	200	400	5.56	3.45	29.39	2.999

## A.2 Code of coord.inpt

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```

5000          'nconfigs'
4             'numspec' number of species
0,F,Zr,Na     'name(i)' name of the species
30,1140,200,400 'natesp(i)' number of atoms of each species
4.7 6.8 5.06 6.4 'rdfmin(i,j)' rdf min for species "i" to species "j".
6.8 6.8 4.9 6.5
5.06 4.9 8.02 9.9
6.4 6.5 9.9 10.2
58.75        box lenght 'boxlen'
5            'numcomb'. Type of analysis 'typecomb(i)'
ca 1 2 0 0 0 ca: coordination analysis (how many 2 there's in each 1)
ls 1 2 3 0 0 ls: linkage state analysis (analyze bridges 1-2-3)
lm 1 0 0 0 0 lm: linkage mechanism analysis (how many 1 linked)
aa 1 2 3 0 0 aa: angle analysis (angle formed by 1 and 3 at the vertex 2)
sh 1 2 0 0 0 sh: sharing analysis (which are the sharing: edge, vertex or
      surface
                    conditions of 2 by each 1)
sc 1 2 0 3 4 sc: selected coordination analysis (how many 2 there's for
      each 1 that have three 4's)
sa 1 2 3 4 5 sa: select angle analysis (angle formed by 1-2-3 restricted to
      the those that have four bridges of the specie 5)
sl 1 2 3 4 5 sl: select linkage state analysis (analyze bridges 1-2-3 for those
      that have four bridges of specie 5)

```

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### A.3 Values of the XFTa : potential

#### A.3.1 Charge-charge interaction

$q_i$  param.

O	-2
F	-1
Zr	+4
Na	+1

#### A.3.2 Overlap repulsion interaction

$a_{ij}$  parameter

	O	F	Zr	Na
O	2.406	2.495	1.589	2.166
F	-	2.444	1.791	1.974
Zr	-	-	5.000	5.000
Na	-	-	-	5.000

$A_{ij}$  parameter

	O	F	Zr	Na
O	290.4	278.4	68.92	221.5
F	-	282.3	72.16	52.83
Zr	-	-	1.000	1.000
Na	-	-	-	1.000

$b_{ij}$  parameter

	O	F	Zr	Na
O	0.850	0.850	1.430	1.144
F	-	10.00	10.00	10.00
Zr	-	-	10.00	10.00
Na	-	-	-	10.00

$B_{ij}$  parameter

	O	F	Zr	Na
O	50000	50000	50000	50000
F	-	0.000	0.000	0.000
Zr	-	-	0.000	0.000
Na	-	-	-	0.000

#### A.3.3 Dispersion interaction

$C_6^{ij}$  parameter

	O	F	Zr	Na
O	44.00	25.70	10.00	4.000
F	-	15.00	33.50	13.25
Zr	-	-	75.00	29.60
Na	-	-	-	11.70

$C_8^{ij}$  parameter

	O	F	Zr	Na
O	853.0	357.7	200.0	50.00
F	-	150.0	335.0	88.15
Zr	-	-	750.0	197.1
Na	-	-	-	51.80

### A.3.4 Polarization interaction

 $f_4^{ij}$  parameter

	O	F	Zr	Na
O	2.513	2.298	2.056	1.964
F	10.00	10.00	1.882	1.831
Zr	1.061	1.882	10.00	10.00
Na	1.964	1.831	10.00	10.00

 $q_i$  Polariz.

O	10.74
F	7.885
Zr	2.926
Na	1.028

1 parameter

	O	F	Zr	Na
O	4.0	4.0	4.0	4.0
F	4.0	4.0	4.0	4.0
Zr	4.0	4.0	4.0	4.0
Na	4.0	4.0	4.0	4.0

2 parameter

	O	F	Zr	Na
O	2.227	2.821	2.420	3.493
F	0.000	0.000	1.886	2.500
Zr	-0.556	-1.000	0.000	0.000
Na	0.066	0.022	0.000	0.000

### A.3.5 Tang-Toenies function values

 $f_6^{ij}$  and  $f_8^{ij}$  parameter

	O	F	Zr	Na
O	1.40	1.65	1.50	1.50
F	-	1.90	1.90	1.90
Zr	-	-	1.90	1.90
Na	-	-	-	1.90

## A.4 Complexes characterization

0.00 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	26.1 % - -	- - -	- - -
1 fluoride	63.9 % 134.4° -	- - -	- - -
2 fluorides	9.8 % 111.3° -	- - -	- - -

0.28 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	22.9 % - -	8.9 % - 125.9°	0.0 % - -
1 fluoride	56.2 % 135.0° -	2.0 % 95.5° 111.3°	0.0 % - -
2 fluorides	9.8 % 111.3° -	0.0 % - -	0.0 % - -

0.56 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	17.2 % - -	17.5 % - 126.0°	0.0 % - -
1 fluoride	52.2 % 134.9° -	3.8 % 95.4° 111.3°	0.0 % - -
2 fluorides	9.0 % 111.3° -	0.1 % - -	0.0 % - -

1.12 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	16.2 % - -	26.3 % - 126.0°	1.0 % - 98.2°
1 fluoride	43.2 % 135.4° -	6.0 % 95.5° 111.4°	0.0 % - -
2 fluorides	7.2 % 111.2° -	0.1 % - -	0.0 % - -

1.69 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	6.9 % - -	38.2 % - 126.0°	0.9 % - 98.2°
1 fluoride	37.9 % 133.2° -	8.7 % 95.5° 111.5°	0.0 % - -
2 fluorides	7.2 % 111.2° -	0.2 % - -	0.0 % - -

3.45 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	9.8 % - -	44.8 % - 126.0°	4.0 % - 98.2°
1 fluoride	27.8 % 136.4° -	9.5 % 95.4° 111.4°	0.0 % - -
2 fluorides	3.9 % 111.1° -	0.2 % - -	0.0 % - -

5.88 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	6.9 % - -	45.8 % - 126.2°	11.9 % - 98.2°
1 fluoride	22.4 % 136.5° -	9.9 % 95.4° 111.6°	0.0 % - -
2 fluorides	2.9 % 110.9° -	0.2 % - -	0.0 % - -

12.50 %mol.O	0 oxygens	1 oxygen	2 oxygens
0 fluorides	5.3 % - -	39.1 % - 125.2°	27.8 % - 95.3°
1 fluoride	17.8 % 136.7° -	8.1 % 95.2° 111.3°	0.1 % - -
2 fluorides	1.6 % 110.5° -	0.1 % - -	0.0 % - -

## A.5 Code of the coord.x program

---

```

!-----
!                               --- Main program ---
!-----

program coord

implicit none

double precision :: boxlen
double precision, allocatable, dimension(:,:) :: rdfmin2

character*2, allocatable, dimension(:) :: namespecie, combtype

integer :: nconfigs, numspecie, numcomb
integer, allocatable, dimension(:) :: natspecie
integer, allocatable, dimension(:,:) :: comb

integer :: i, j

open(10, file='coord.inpt')

read(10,*) nconfigs
read(10,*) numspecie

allocate
    (namespecie(numspecie), natspecie(numspecie), rdfmin2(numspecie, numspecie))

read(10,*) (namespecie(i), i=1, numspecie)
read(10,*) (natspecie(i), i=1, numspecie)

do i=1, numspecie
    read(10,*) (rdfmin2(i, j), j=1, numspecie)
    do j=1, numspecie
        rdfmin2(i, j) = rdfmin2(i, j) ** 2
    enddo
enddo

read(10,*) boxlen
read(10,*) numcomb

allocate (comb(numcomb, 5), combtype(numcomb))

do i=1, numcomb
    read(10,*) combtype(i), comb(i, 1), comb(i, 2), comb(i, 3), comb(i, 4), comb(i, 5)
enddo

call ouverture(numcomb, comb, combtype)
call loop(boxlen, rdfmin2, nconfigs, numcomb, combtype, numspecie, comb, &
    natspecie, namespecie)
call closing(numcomb)

end program coord

```

```

!-----
!               --- Opening subroutine ---
!-----

subroutine ouverture(numcomb,comb,combtype)

implicit none

integer, intent(in) :: numcomb
integer, intent(in), dimension(numcomb,5) :: comb
character*2, intent(in),dimension(numcomb) :: combtype
character*40 :: fileout
integer :: i

do i=1,numcomb
  if (combtype(i)=='ca') then
    fileout='coord_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='ls') then
    fileout='linkage_state_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//&
      char(comb(i,3)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='lm') then
    fileout='linkage_mechanism_analysis'//char(comb(i,1)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='aa') then
    fileout='angle_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//&
      char(comb(i,3)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='sh') then
    fileout='share_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='sc') then
    fileout='select_coord_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//&
      char(comb(i,4)+48)//char(comb(i,5)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='sa') then
    fileout='select_angle_analysis'//char(comb(i,1)+48)//char(comb(i,2)+48)//&
      char(comb(i,3)+48)//char(comb(i,4)+48)//&
      char(comb(i,5)+48)//'.dat'
    open(20+i,file=fileout)
  elseif (combtype(i)=='sl') then
    fileout='select_linkage_state_analysis'//char(comb(i,1)+48)//&
      char(comb(i,2)+48)//&
      char(comb(i,3)+48)//&
      char(comb(i,4)+48)//&
      char(comb(i,5)+48)//'.dat'
    open(20+i,file=fileout)
  endif
enddo

end subroutine ouverture

```

```

!-----
!               --- Main loop subroutine ---
!-----

subroutine loop(boxlen,rdfmin2,nconfigs,numcomb,&
               combtype,numspecie,comb,natspecie,namespecie)

implicit none

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2

integer, intent(in) :: nconfigs,numcomb,numspecie
integer, intent(in), dimension(numcomb,5) :: comb
integer, intent(in), dimension(numspecie) :: natspecie

character*2, intent(in), dimension (numspecie) :: namespecie
character*2, intent(in), dimension (numcomb) :: combtype

double precision, allocatable, dimension(:,:) :: x,y,z
integer, dimension(180) :: numangle
integer, dimension(0:30) :: num

integer :: natmax,npair,i,j

natmax=0
do i=1,numspecie
    natmax=max(natmax,natspecie(i))
enddo
allocate (x(numspecie,natmax),y(numspecie,natmax),z(numspecie,natmax))

do i=1,numcomb
    write(6,*) 'Starting analisys #',i
    call reset(num,npair,numangle)
    open(10,file='../positions.out')
    do j=1,nconfigs
        if(mod(j,100) == 0) write(6,*) j
        call resetpos(numspecie,x,y,z,natmax)
        call readpositions(comb(i,1),comb(i,2),comb(i,3),comb(i,5),numspecie,&
                           x,y,z,natspecie,natmax)
        if (combtype(i) == 'ca') call
            coordloop(comb(i,1),comb(i,2),x,y,z,natspecie,&
                    num,boxlen,rdfmin2,numspecie,natmax)
        if (combtype(i) == 'ls') call linkstateloop(comb(i,1),comb(i,2),comb(i,3),&
            x,y,z,natspecie,boxlen,&
            rdfmin2,npair,num,numspecie,natmax)
        if (combtype(i) == 'lm') call linkmechloop(comb(i,1),x,y,z,natspecie,num,&
            boxlen,rdfmin2,npair,numspecie,natmax)
        if (combtype(i) == 'aa') call
            angleloop(comb(i,1),comb(i,2),comb(i,3),x,y,z,&
                    natspecie,boxlen,&
                    rdfmin2,npair,numspecie,natmax,numangle)
        if (combtype(i) == 'sh') call
            sharingloop(comb(i,1),comb(i,2),x,y,z,natspecie,&
                    boxlen,rdfmin2,&

```

```

                                npair,numspecie,natmax,num)
if (combtype(i) == 'sc') call
    selectcoordloop(comb(i,1),comb(i,2),comb(i,4),&
                                comb(i,5),x,y,z,natspecie,num,&
                                boxlen,rdfmin2,npair,numspecie,natmax)
if (combtype(i) == 'sa') call
    selectangleloop(comb(i,1),comb(i,2),comb(i,3),&
                                comb(i,4),comb(i,5),x,y,z,&
                                natspecie,boxlen,rdfmin2,npair,&
                                numspecie,natmax,numangle)
if (combtype(i) == 'sl') call
    selectlinkstateloop(comb(i,1),comb(i,2),comb(i,3),&
                                comb(i,4),comb(i,5),x,y,z,&
                                natspecie,boxlen,rdfmin2,npair,&
                                num,numspecie,natmax)
enddo
close(10)
if (combtype(i) == 'ca') call
    coordnorm(comb(i,1),comb(i,2),i,namespecie,numspecie,&
                                natspecie,num,nconfigs)
if (combtype(i) == 'ls') call linkstatenorm(comb(i,1),comb(i,2),comb(i,3),i,&
                                namespecie,numspecie,num,npair)
if (combtype(i) == 'lm') call
    linkmechnorm(comb(i,1),i,namespecie,numspecie,num,npair)
if (combtype(i) == 'aa') call
    anglenorm(comb(i,1),comb(i,2),comb(i,3),i,namespecie,&
                                numspecie,numangle,npair)
if (combtype(i) == 'sh') call
    sharenorm(comb(i,1),comb(i,2),i,namespecie,numspecie,&
                                num,npair)
if (combtype(i) == 'sc') call selectcoordnorm(comb(i,1),comb(i,2),comb(i,4),&
                                comb(i,5),i,namespecie,numspecie,&
                                natspecie,num,npair)
if (combtype(i) == 'sa') call
    anglenorm(comb(i,1),comb(i,2),comb(i,3),i,namespecie,&
                                numspecie,numangle,npair)
if (combtype(i) == 'sl') call
    selectlinkstatenorm(comb(i,1),comb(i,2),comb(i,3),&
                                comb(i,4),comb(i,5),&
                                i,namespecie,numspecie,num,npair)

write(6,*) 'Finishing analisys #',i
write(6,*) ' ---- '
enddo

end subroutine loop

```



```
!-----  
!               --- Reset subroutines ---  
!-----  
  
subroutine reset(num,npair,numangle)  
  
implicit none  
  
integer, intent(inout) :: npair  
integer, intent(inout), dimension(0:30) :: num  
integer, intent(inout), dimension(180) :: numangle  
  
integer :: i  
  
npair = 0  
  
do i=0,30  
    num(i)=0  
enddo  
  
do i=1,180  
    numangle(i)=0  
enddo  
  
end subroutine reset  
  
!-----  
  
subroutine resetpos(numspecie,x,y,z,natmax)  
  
implicit none  
  
integer, intent(in) :: numspecie,natmax  
  
double precision, intent(inout), dimension(numspecie,natmax) :: x,y,z  
  
integer :: i,j  
  
do i=1,numspecie  
    do j=1,natmax  
        x(i,j)=0.0  
        y(i,j)=0.0  
        z(i,j)=0.0  
    enddo  
enddo  
  
end subroutine resetpos
```

```

!-----
!               --- Positions reading subroutine ---
!-----

subroutine readpositions(specie1,specie2,specie3,specie4,numspecie,x,y,z, &
                        natspecie,natmax)

implicit none

!It's important to stress that the positions to read are stocked
!in comb(i,j) where j=1,2,3and5. comb(i,4) must be always reserved
!to indicate the conditions.

integer, intent(in) :: numspecie,specie1,specie2,specie3,specie4,natmax
integer, intent(in), dimension(numspecie) :: natspecie
double precision, intent(inout), dimension(numspecie,natmax) :: x,y,z

integer :: i,j

do i=1,numspecie
  if (i==specie1 .or. i==specie2 .or. i==specie3 .or. i==specie4) then
    do j=1,natspecie(i)
      read(10,*) x(i,j),y(i,j),z(i,j)
    enddo
  else
    do j=1,natspecie(i)
      read(10,*)
    enddo
  endif
enddo

end subroutine readpositions

!-----
!               --- Analysis subroutines ---
!-----

subroutine coordloop(specie1,specie2,x,y,z,natspecie,num,boxlen,rdfmin2,&
                    numspecie,natmax)

implicit none

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

integer, intent(in) :: numspecie,natmax,specie1,specie2
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout), dimension(0:30) :: num

double precision :: sqr12

integer :: ncoord
integer :: i,j

```

```

do i=1,natspecie(specie1)
  ncoord=0
  do j=1,natspecie(specie2)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                x(specie2,j),y(specie2,j),z(specie2,j),sqr12,boxlen)
    if (sqr12 == 0.0) cycle
    if (sqr12 < rdfmin2(specie1,specie2)) ncoord=ncoord+1
  enddo
  num(ncoord)=num(ncoord)+1
enddo

end subroutine coordloop

!-----

subroutine
  linkstateloop(specie1,specie2,specie3,x,y,z,natspecie,boxlen,rdfmin2,npair,&
               num,numspecie,natmax)

implicit none

integer, intent(in) :: specie1,specie2,specie3,numspecie,natmax
integer, intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout), dimension(0:30) :: num

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

double precision :: sqr13,sqr12,sqr23

integer :: nshar
integer :: i,j,k

do i=1,natspecie(specie1)
  do j=1,natspecie(specie3)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                x(specie3,j),y(specie3,j),z(specie3,j),sqr13,boxlen)
    if (sqr13 == 0.0) cycle
    if (sqr13 < rdfmin2(specie1,specie3)) then
      nshar = 0
      do k=1,natspecie(specie2)
        call findsqr(x(specie2,k),y(specie2,k),z(specie2,k),&
                    x(specie1,i),y(specie1,i),z(specie1,i),sqr12,boxlen)
        call findsqr(x(specie2,k),y(specie2,k),z(specie2,k),&
                    x(specie3,j),y(specie3,j),z(specie3,j),sqr23,boxlen)
        if ((sqr12 < rdfmin2(specie1,specie2)) .and. &
            (sqr23 < rdfmin2(specie2,specie3))) nshar=nshar+1
      enddo
      num(nshar) = num(nshar) + 1
      npair = npair + 1
    endif
  enddo
enddo

```

```
end subroutine linkstateloop
```

```
!-----
```

```
subroutine linkmechloop(specie1,x,y,z,natspecie,num,boxlen,rdfmin2,&
                        npair,numspecie,natmax)
```

```
implicit none
```

```
integer, intent(in) :: specie1,numspecie,natmax
integer,intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout), dimension(0:30) :: num
```

```
double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z
```

```
double precision :: sqr11
```

```
integer :: ncoord
integer :: i,j
```

```
do i=1,natspecie(specie1)
  ncoord=0
  do j=1,natspecie(specie1)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                x(specie1,j),y(specie1,j),z(specie1,j),sqr11,boxlen)
    if (sqr11 == 0.0) cycle
    if (sqr11 < rdfmin2(specie1,specie1)) ncoord=ncoord+1
  enddo
  num(ncoord)=num(ncoord)+1
  npair = npair + 1
enddo
```

```
end subroutine linkmechloop
```

```
!-----
```

```
subroutine angleloop(specie1,specie2,specie3,x,y,z,natspecie,boxlen,rdfmin2,&
                    npair,numspecie,natmax,numangle)
```

```
implicit none
```

```
integer, intent(in) :: specie1,specie2,specie3,numspecie,natmax
integer,intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout),dimension(180) :: numangle
```

```
double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z
```

```
double precision :: sqr12,sqr13,sqr23,angle
```

```

integer :: i,j,k

do i=1,natspecie(specie1)
  do j=1,natspecie(specie3)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                 x(specie3,j),y(specie3,j),z(specie3,j),sqr13,boxlen)
    if (sqr13 == 0.0) cycle
    if (sqr13 < rdfmin2(specie1,specie3)) then
      do k=1,natspecie(specie2)
        call findsqr(x(specie2,k),y(specie2,k),z(specie2,k),&
                     x(specie1,i),y(specie1,i),z(specie1,i),sqr12,boxlen)
        call findsqr(x(specie2,k),y(specie2,k),z(specie2,k),&
                     x(specie3,j),y(specie3,j),z(specie3,j),sqr23,boxlen)
        if ((sqr12<rdfmin2(specie1,specie2)) .and.&
            (sqr23<rdfmin2(specie2,specie3))) then
          angle = 0.0d0
          call findangle(x(specie2,k),y(specie2,k),z(specie2,k),&
                        x(specie3,j),y(specie3,j),z(specie3,j),&
                        x(specie1,i),y(specie1,i),z(specie1,i),angle,boxlen)
          numangle(int(angle))=numangle(int(angle))+1
          npair = npair + 1
        endif
      enddo
    endif
  enddo
enddo

end subroutine angleloop

!-----

subroutine sharingloop(specie1,specie2,x,y,z,natspecie,boxlen,rdfmin2,&
                      npair,numspecie,natmax,num)

implicit none

integer, intent(in) :: specie1,specie2,numspecie,natmax
integer,intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout),dimension(0:30) :: num

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

double precision :: sqr121,sqr122,sqr11

integer :: counter

integer :: i,j,k

do i=1,natspecie(specie1)
  do j=1,natspecie(specie1)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&

```

```

        x(specie1,j),y(specie1,j),z(specie1,j),sqr11,boxlen)
if (sqr11 == 0.0) cycle
if (sqr11 < rdfmin2(specie1,specie1)) then
  counter = 0
  do k=1, natspecie(specie2)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
      x(specie2,k),y(specie2,k),z(specie2,k),sqr121,boxlen)
    call findsqr(x(specie1,j),y(specie1,j),z(specie1,j),&
      x(specie2,k),y(specie2,k),z(specie2,k),sqr122,boxlen)
    if ((sqr121 < rdfmin2(specie1,specie2)) .and. &
      (sqr122 < rdfmin2(specie1,specie2))) counter = counter + 1
  enddo
  num(counter) = num(counter)+1
  npair = npair + 1
endif
enddo
enddo

end subroutine sharingloop

!-----

subroutine selectcoordloop(specie1,specie2,condition,specie3,x,y,z,natspecie,&
  num,boxlen,rdfmin2,npair,numspecie,natmax)

implicit none

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

integer, intent(in) :: numspecie,natmax,specie1,specie2,specie3,condition
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout) :: npair
integer, intent(inout), dimension(0:30) :: num

double precision :: sqr21,sqr13

integer :: ncoord,counter
integer :: i,j

do i=1,natspecie(specie1)
  counter=0
  do j=1,natspecie(specie3)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
      x(specie3,j),y(specie3,j),z(specie3,j),sqr13,boxlen)
    if (sqr13 < rdfmin2(specie1,specie3)) then
      counter = counter + 1
    endif
  enddo
  if (counter == condition) then
    ncoord=0
    do j=1,natspecie(specie2)
      call findsqr(x(specie2,j),y(specie2,j),z(specie2,j),&
        x(specie1,i),y(specie1,i),z(specie1,i),sqr21,boxlen)

```

```

        if (sqr21 < rdfmin2(specie2,specie1)) ncoord=ncoord+1
    enddo
    num(ncoord)=num(ncoord)+1
    npair=npair+1
endif
enddo

end subroutine selectcoordloop

!-----

subroutine
    selectangleloop(specie1,specie2,specie3,condition,specie4,x,y,z,natspecie,&
                    boxlen,rdfmin2,npair,numspecie,natmax,numangle)

implicit none

integer, intent(in) :: specie1,specie2,specie3,specie4,numspecie,natmax,condition
integer,intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout),dimension(180) :: numangle

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

double precision :: sqr13,sqr14,sqr34,sqr12,sqr32,angle
integer :: i,j,k,l,nshar

do i=1,natspecie(specie1)
    do j=1,natspecie(specie3)
        call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                    x(specie3,j),y(specie3,j),z(specie3,j),sqr13,boxlen)
        if (sqr13 == 0.0) cycle
        if (sqr13 < rdfmin2(specie1,specie3)) then
            nshar = 0
            do k=1,natspecie(specie4)
                call findsqr(x(specie4,k),y(specie4,k),z(specie4,k),&
                            x(specie1,i),y(specie1,i),z(specie1,i),sqr14,boxlen)
                call findsqr(x(specie4,k),y(specie4,k),z(specie4,k),&
                            x(specie3,j),y(specie3,j),z(specie3,j),sqr34,boxlen)
                if ((sqr14<rdfmin2(specie1,specie4)) .and.
                    (sqr34<rdfmin2(specie3,specie4))) nshar = nshar + 1
            enddo
        enddo
    enddo
!-----Calculate JUST the angle of the 'condition' number of bridges
    if (nshar == condition) then
        do l=1,natspecie(specie2)
            call findsqr(x(specie2,l),y(specie2,l),z(specie2,l),&
                        x(specie1,i),y(specie1,i),z(specie1,i),sqr12,boxlen)
            call findsqr(x(specie2,l),y(specie2,l),z(specie2,l),&
                        x(specie3,j),y(specie3,j),z(specie3,j),sqr32,boxlen)
            if ((sqr12<rdfmin2(specie1,specie2)) .and. &
                (sqr32<rdfmin2(specie3,specie2))) then
                angle = 0.0d0
                call findangle(x(specie2,l),y(specie2,l),z(specie2,l),&

```

```

                                x(specie3,j),y(specie3,j),z(specie3,j),&
                                x(specie1,i),y(specie1,i),z(specie1,i),angle,boxlen)
                                numangle(int(angle))=numangle(int(angle))+1
                                endif
                                enddo
                                endif
                                npair=npair+1
!-----
                                endif
                                enddo
                                enddo

end subroutine selectangleloop

!-----

subroutine selectlinkstateloop(specie1,specie2,specie3,condition,specie4,x,y,z,&
                                natspecie,boxlen,rdfmin2,npair,num,numspecie,natmax)

implicit none

integer, intent(in) :: specie1,specie2,specie3,specie4,condition,numspecie,natmax
integer, intent(inout) :: npair
integer, intent(in), dimension(numspecie) :: natspecie
integer, intent(inout), dimension(0:30) :: num

double precision, intent(in) :: boxlen
double precision, intent(in), dimension(numspecie,numspecie) :: rdfmin2
double precision, intent(in), dimension(numspecie,natmax) :: x,y,z

double precision :: sqr31,sqr14,sqr34,sqr12,sqr32

integer :: nsharaux,nshar
integer :: i,j,k,l

do i=1,natspecie(specie1)
  do j=1,natspecie(specie3)
    call findsqr(x(specie1,i),y(specie1,i),z(specie1,i),&
                 x(specie3,j),y(specie3,j),z(specie3,j),sqr31,boxlen)
    if (sqr31 == 0.0) cycle
    if (sqr31 < rdfmin2(specie3,specie1)) then
      nsharaux=0
      do k=1,natspecie(specie4)
        call findsqr(x(specie4,k),y(specie4,k),z(specie4,k),&
                     x(specie1,i),y(specie1,i),z(specie1,i),sqr14,boxlen)
        call findsqr(x(specie4,k),y(specie4,k),z(specie4,k),&
                     x(specie3,j),y(specie3,j),z(specie3,j),sqr34,boxlen)
        if ((sqr14 < rdfmin2(specie1,specie4)) .and. &
            (sqr34 < rdfmin2(specie3,specie4))) nsharaux=nsharaux+1
      enddo
!-----Calculate JUST the linkage state of the 'condition' number of
      bridges
      if (nsharaux == condition) then
        nshar=0
        do l=1,natspecie(specie2)

```



```

        call findsqr(x(specie2,l),y(specie2,l),z(specie2,l),&
                     x(specie1,i),y(specie1,i),z(specie1,i),sqr12,boxlen)
        call findsqr(x(specie2,l),y(specie2,l),z(specie2,l),&
                     x(specie3,j),y(specie3,j),z(specie3,j),sqr32,boxlen)
        if ((sqr12<rdfmin2(specie1,specie2)) .and. &
            (sqr32<rdfmin2(specie3,specie2))) nshar=nshar+1
    enddo
    num(nshar) = num(nshar) + 1
endif
npair=npair+1
!-----
    endif
    enddo
enddo

end subroutine selectlinkstateloop

!-----
!               --- Normalisation subroutines ---
!-----

subroutine
    coordnorm(specie1,specie2,i,namespecie,numspecie,natspecie,num,nconfigs)

implicit none

integer, intent(in) :: i,nconfigs,specie1,specie2,numspecie
integer, intent(in), dimension(0:30) :: num
integer, intent(in), dimension(numspecie) :: natspecie

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

check=0.0
write(20+i,*) 'Coordination_analysis ',namespecie(specie1),' -
              ',namespecie(specie2)
do j=0,30
    if (num(j) /= 0) then
        write(20+i,*)'#',j, 'coord', 100.0*(float(num(j))/&
            float(nconfigs*natspecie(specie1)))
        check=check+(float(num(j))/float(nconfigs*natspecie(specie1)))
    endif
enddo
write(20+i,*)'# check',check*100.0

end subroutine coordnorm

!-----

subroutine
    linkstatenorm(specie1,specie2,specie3,i,namespecie,numspecie,num,npair)

implicit none

```

```

integer, intent(in) :: i,specie1,specie2,specie3,numspecie,npair
integer, intent(in), dimension(0:30) :: num

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

check = 0.0
write(20+i,*) 'Linkage_stat_analysis ',namespecie(specie1),' - ',&
              namespecie(specie2),' - ',namespecie(specie3)
do j=0,30
  if (num(j) /= 0) then
    write(20+i,*) j,'time/s connected',100.0*float(num(j))/float(npair)
    check=check+float(num(j))
  endif
enddo
write(20+i,*)
write(20+i,*) 'check',100.0*check/float(npair)

end subroutine linkstatenorm

!-----

subroutine linkmechnorm(specie1,i,namespecie,numspecie,num,npair)

implicit none

integer, intent(in) :: i,specie1,numspecie,npair
integer, intent(in), dimension(0:30) :: num

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

write(20+i,*) 'Linkage_mechanism_analysis ',namespecie(specie1)
check=0.0
do j=0,30
  if (num(j) /= 0) then
    write(20+i,*) '#',j,'links',100.0*float(num(j))/float(npair)
    check=check+float(num(j))
  endif
enddo
write(20+i,*)
write(20+i,*) 'check',100.0*check/float(npair)

end subroutine linkmechnorm

!-----

subroutine
  anglenorm(specie1,specie2,specie3,i,numspecie,namespecie,numangle,npair)

```

```

implicit none

integer, intent(in) :: i,specie1,specie2,specie3,numspecie,npair
integer, intent(in), dimension(180) :: numangle

character*2, intent(in),dimension(numspecie) :: namespecie

integer :: j

do j=1,180
  if (numangle(j) /= 0) then
    write(20+i,*) j,100.0*float(numangle(j))/float(npair)
  endif
enddo

end subroutine anglenorm

!-----

subroutine sharenorm(specie1,specie2,i,namespecie,numspecie,num,npair)

implicit none

integer, intent(in) :: i,specie1,specie2,numspecie,npair
integer, intent(in), dimension(0:30) :: num

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

check=0.0

write(20+i,*) 'Sharing analysis ',namespecie(specie1),' - ',&
              namespecie(specie2),'(shared one)'

write(20+i,*) '#   Sharing anything',100.0*float(num(0))/float(npair)
write(20+i,*) '#   Corner sharing ',100.0*float(num(1))/float(npair)
write(20+i,*) '#   Edge sharing  ',100.0*float(num(2))/float(npair)
write(20+i,*) '#   Face sharing  ',100.0*float(num(3))/float(npair)

do j=0,3
  check=check+(float(num(j))/float(npair))
enddo

write(20+i,*) '# Check',check*100.0

end subroutine sharenorm

!-----

subroutine selectcoordnorm(specie1,specie2,condition,specie3,i,namespecie,&
                           numspecie,natspecie,num,npair)

implicit none

```

```

integer, intent(in) :: i,specie1,specie2,specie3,condition,numspecie,npair
integer, intent(in), dimension(0:30) :: num
integer, intent(in), dimension(numspecie) :: natspecie

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

check=0.0
write(20+i,*) 'Select_coordination_analysis ',namespecie(specie1),' - ',&
namespecie(specie2),' restricted to ',condition,' -
',namespecie(specie3)
do j=0,30
  if (num(j) /= 0) then
    write(20+i,*)'#',j, 'coord', 100.0*(float(num(j))/float(npair))
    check=check+(float(num(j))/float(npair))
  endif
enddo
write(20+i,*)'# check',check*100.0

end subroutine selectcoordnorm

!-----

subroutine selectlinkstatenorm(specie1,specie2,specie3,condition,specie4,&
i,namespecie,numspecie,num,npair)

implicit none

integer, intent(in) ::
  i,specie1,specie2,specie3,specie4,condition,numspecie,npair
integer, intent(in), dimension(0:30) :: num

character*2, intent(in),dimension(numspecie) :: namespecie

double precision :: check
integer :: j

check = 0.0
write(20+i,*) 'Select_linkage_stat_analysis ',&
namespecie(specie1),' - ',namespecie(specie2),' -
',namespecie(specie3),&
' restricted to',condition,' - ',namespecie(specie4)
do j=0,30
  if (num(j) /= 0) then
    write(20+i,*) j,'time/s connected',100.0*float(num(j))/float(npair)
    check=check+float(num(j))
  endif
enddo
write(20+i,*)
write(20+i,*) 'check',100.0*check/float(npair)

end subroutine selectlinkstatenorm

```

```

!-----
!               --- Recursive subroutines ---
!-----

subroutine findsqr(xesp1,yesp1,zesp1,xesp2,yesp2,zesp2,sqr,boxlen)

double precision, intent(in) :: xesp1,yesp1,zesp1,xesp2,yesp2,zesp2,boxlen
double precision, intent(out) :: sqr
double precision :: dx,dy,dz,halfboxrec

halfboxrec=1.d0/(boxlen/2.0d0)
dx=xesp2-xesp1
dy=yesp2-yesp1
dz=zesp2-zesp1
dx=dx-boxlen*int(dx*halfboxrec)
dy=dy-boxlen*int(dy*halfboxrec)
dz=dz-boxlen*int(dz*halfboxrec)
sqr=dx**2+dy**2+dz**2

end subroutine findsqr

!-----

subroutine findangle(x1,y1,z1,x2,y2,z2,x3,y3,z3,angle,boxlen)

double precision, intent(in) :: boxlen
double precision, intent(in) :: x1,y1,z1 !---1 must be always the vertex---!
double precision, intent(in) :: x2,y2,z2,x3,y3,z3
double precision, intent(inout) :: angle
double precision :: p12,p23,p13,pi

pi = 2*ACOS(0.0d0)

call findsqr(x1,y1,z1,x2,y2,z2,p12,boxlen)
call findsqr(x1,y1,z1,x3,y3,z3,p13,boxlen)
call findsqr(x2,y2,z2,x3,y3,z3,p23,boxlen)

angle = 180*(acos((p12+p13-p23)/(2*sqrt(p12)*sqrt(p13))))/pi

end subroutine findangle

!-----
!               --- Closing subroutine ---
!-----

subroutine closing(numcomb)

integer, intent(in) :: numcomb
integer :: i

do i=1,numcomb
  close(20+i)
enddo

end subroutine closing

```



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# Bibliographie

- [1] R. Livingston. The next generation. *Nuclear Industry*, July 1988.
- [2] S. Delpech, E. Merle-Lucotte, D. Heuer, M. Allibert, V. Ghetta, C. Le-Brun, X. Dodeligez, and G. Picard. Reactor physic and reprocessing scheme for innovative molten salt reactor system. *Journal of Fluorine Chemistry*, 130(1) :11–17, January 2009.
- [3] C Forsberg. The advanced high-temperature reactor : high-temperature fuel, liquid salt coolant, liquid-metal-reactor plant. *Progress in Nuclear Energy*, 47(1-4, SI) :32–43, 2005. 1st COE-INES International Symposium (INES-1), Tokyo, JAPAN, OCT 31-NOV 04, 2004.
- [4] H. Moriyama, A. Sagara, S. Tanaka, R.W. Moir, and D.K. Sze. Molten salts in fusion nuclear technology. *Fusion Engineering and Design*, 39-40 :627–637, 1998.
- [5] R.W. Moir. Cost of electricity from molten salt reactors (msr). *Nuclear Technology*, 138 :93–95, 2002.
- [6] C. Le Brun. Molten salts and nuclear energy production. *Journal of Nuclear Materials*, 360(1) :1–5, January 2005.
- [7] Vladimir Khokhlov, Victor Ignatiev, and Valery Afonichkin. Evaluating physical properties of molten salt reactor fluoride mixtures. *Journal of Fluorine Chemistry*, 130(1) :30–37, 2009.
- [8] D. F. Williams, L. M. Toth, and K. T. Clarno. Assessment of candidate molten salt coolants for the advanced high-temperature reactor (ahtr). Ornl/tm-2006/12, OAK Ridge National Laboratory, March 2006.
- [9] O. Pauvert, D. Zanghi, M. Salanne, C. Simon, A. Rakhmatullin, H. Matsuura, Yoshihiro Okamoto, Francois Vivet, and C. Bessada. In situ experimental evidence for a nonmonotonous structural evolution with composition in the molten lif-zrf(4) system. *Journal of Physical Chemistry B*, 114(19) :6472–6479, 2010.
- [10] O. Pauvert, M. Salanne, D. Zanghi, C. Simon, S. Reguer, D. Thiaudiere, Y. Okamoto, H. Matsuura, and C. Bessada. Ion specific effects on the structure of molten af-zrf(4) systems (a(+) = li(+), na(+), and k(+)). *Journal of Physical Chemistry B*, 115(29) :9160–9167, 2011.
- [11] V. Dracopoulos, J. Vagelatos, and G.N. Papatheodorou. Raman spectroscopic studies of molten zrf4-kf mixtures and of a(2)zrf(6), a(3)zrf(7) (a = li, k or cs) compounds. *Journal of the Chemical Society-Dalton transactions*, 7 :1117–1122, 2001.
- [12] D. Marrocchelli, M. Salanne, P. A. Madden, C. Simon, and P. Turq. The construction of a reliable potential for geo2 from first principles. *Molecular Physics*, 107(4-6) :443–452, 2009.
- [13] M.P. Allen and D.J. Tildesley. *Computer Simulation of Liquids*. Oxford Science Publications, Oxford, 1987.

- [14] D. Frenkel and B. Smit. *Understanding Molecular Simulation. From Algorithms to Applications*, volume 1. Computational Science Series, Elsevier (USA), second édition edition, 2002.
- [15] A. R. Leach. *Molecular Modelling. Principles and Applications*. Second edition. Pearson Education Limited, Harlow, 2001.
- [16] R.J. Heaton. *From First Principles to Material Properties*. PhD thesis, University of Oxford, Oxford, 2007.
- [17] S. Viscardy and P. Gaspard. Viscosity in molecular dynamics with periodic boundary conditions. *Physical Review Letters*, 68, October 2003.
- [18] Siska P.E. A modified tang-toennies model for ion-atom potential curves. *The Journal of Chemical Physics*, 85(12) :7497–7498, December 1986.
- [19] M. Salanne, B. Rotenberg, S. Jahn, R. Vuilleumier, C. Simon, and P. A. Madden. Including many-body effects in models for ionic liquids. *Theoretical Chemistry Accounts*, 131(3), March 2012.
- [20] O. Pauvert. *Etude structurale de sels fondus d'intérêts nucléaires par RMN et EXAFS haute température*. PhD thesis, Université Orléans, 2009.
- [21] J. Hives and J. Thonstad. Electrical conductivity of low-melting electrolytes for aluminium smelting. *Electrochimica Acta*, 49 :5111–5114, 2004.
- [22] G J Janz, F W Dampier, G R Lakshminarayanan, P K Lorenz, and R P T Tomkins. *Molten Salts. Volume I. Electrical Conductance, Density, and Viscosity Data*. National Standard Reference Data System, October 1968.